

beryl, which, as has been stated earlier, satisfy approximately the conditions required for central forces. The general shape of the contours changes as one proceeds outwards from a reciprocal-lattice point.

There are no signs of the very strong streaks connecting the Laue spots, which have been reported by Lonsdale (1946) for the case of ice and ammonium fluoride. This would suggest that the origin of these streaks (Born, 1946) is not due to the ordinary thermal motion, but to the existence, in these crystals, of atoms, which have two possible positions of equilibrium. In the case of ice, the hydrogen atoms are assumed to lie on a line joining two oxygen atoms. The equilibrium position of the hydrogen atom is not at the midpoint of this line, but nearer to either one or the other of the oxygen atoms. A survey of the evidence for this is given in a paper by Penny (1947). A statistical distribution of the hydrogen atoms over these two positions would, as Born has shown, give rise to a continuous distribution of scattering power in reciprocal space.

It is to be noted that the chart cannot be extended indefinitely in Q -space, for the general formula (1.6), for the scattering power, is valid only for points of Q -space which are not too far from the origin. This distance depends on the temperature. A full discussion of the validity of the general theory is given in the report by Born (1942-3).

Finally it should be remembered that the calculation has been made using a model in which only the forces between next neighbours are considered. The neglect of long-range forces will be of little influence for long waves

(corresponding Q -vectors will lie near a reciprocal-lattice point), but will be very essential for waves of the same order of length as the lattice constant. Thus, in the case of an ionic lattice, where long-range forces are important, the value obtained above for the isodiffusion function for those wave vectors Q which lie in the region between the reciprocal-lattice points can be regarded only as a first approximation. As has been stated by Begbie (1947), the reason for using a model, which certainly is not a good picture of reality, is that the method of next neighbours can be generalized; it can be used for all kinds of substances, and all kinds of symmetry.

I wish to take this opportunity of expressing my gratitude to Prof. Born for suggesting this problem to me and for his advice during the progress of the work.

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Acta Cryst. (1949). **2**, 333

Morphological and Dielectric Studies of some Crystals of the Rochelle Salt Type

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Observations have been made on the morphology of crystals of the Rochelle salt type, with particular reference to the effects of added impurities. Certain noteworthy changes of habit have been recorded. Measurements have also been made on the inductivities of about ninety specimens of these crystals, at room temperature, throughout the range of frequency from 650 to 2650 kcyc.sec.⁻¹.

While individual values were found not to vary at these frequencies, the inductivities showed a marked dependence on composition and on the presence of cupric ions, boric acid, or the ammonium radical.

Introduction

The crystals of the type of Rochelle salt, with whose inductivities this paper is concerned, may be considered as being derivatives of the original sodium potassium tartrate tetrahydrate (Rochelle salt), in which either

the relative amounts of sodium and potassium have been changed or one of these metals has been substituted by a new metallic radical. Crystals of each type were also grown with a habit-modifying addition in the solution.

The habits of these series of crystals, together with some of their physical characteristics, were investigated some years ago by Buckley (1924). One of his more interesting observations dealt with the changes in habit which were caused by the introduction of impurities to the liquor.

In view of the remarkable electrical properties of Rochelle salt, which shows very great anisotropy, experiments were done to determine the extent of this anisotropy in the other series, with the object of relating the findings, if possible, to the habit and structure of the crystals.

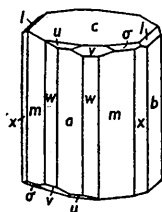


Fig. 1.

Fig. 1. Hypothetical 'mean' crystal.

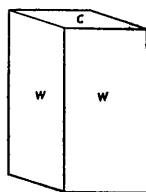


Fig. 2.

Fig. 2. Change in habit caused by the addition of cupric ions to Rochelle salt.

Fig. 1 represents a hypothetical crystal, showing the average of the variations found in the different series. No member is exactly like this; for instance, it is only in sodium ammonium tartrate that the face x , $\{120\}$, ever assumes the prominence given here, whilst it is absent in the pure Rochelle salt. Again, the face b , $\{010\}$, scarcely varies throughout the whole series, whereas the face a , $\{100\}$, is far more important in Rochelle salt than in the sodium ammonium tartrate. There is an indication that the ammonium radical does not take kindly to the $\{100\}$ faces, as in the above case, while, when excess sodium tartrate is present in the solution of sodium ammonium tartrate, $\{100\}$ becomes the predominant face, chiefly at the expense of $\{110\}$; but when there is excess of ammonium (as tartrate) the $\{100\}$ face disappears. In further corroboration, the salt $(50\text{NH}_4\text{Na}.50\text{NH}_4\text{K})\text{T}$, which may be rewritten as $(50\text{KNa}.50(\text{NH}_4)_2)\text{T}$, also has no $\{100\}$ face, whereas this face is strongly developed in the pure Rochelle salt— $(\text{KNa})\text{T}$ —as stated previously. The letter T will be used where necessary as the abbreviation for 'tartrate'.

Apart from the marked predominance of $\{110\}$ on $(50\text{NH}_4\text{Na}.50\text{NH}_4\text{K})\text{T}$, there are no other changes of note in the various mixtures, until unrelated impurities begin to be added. The most noticeable of such induced changes may be seen from Fig. 2, which shows the result of adding cupric ion to Rochelle salt, and it is a change which is confined to Rochelle salt alone. The compound $(50\text{KNa}.50\text{KK})\text{T}$ is very similar in habit to the pure Rochelle salt, but the effect of the addition of the cupric ion is to cause flattening of the basal plane (see Fig. 3).

If boric acid is used instead of cupric ion, the change in habit of Rochelle salt is the same as that produced by the cupric ion, although it is no longer the same for the $(50\text{KNa}.50\text{KK})$ tartrate. The noteworthy features of crystals grown in the presence of boric acid, apart from their inductivity which will be mentioned later, are their clearness, compactness, and great toughness as compared with the easily cleaved pure Rochelle salt. These crystals showed no sign of dendrite growth, and had only very small inclusions, pointing to the supposition that they had been constrained to grow in some quite different way, in comparison with Rochelle salt.

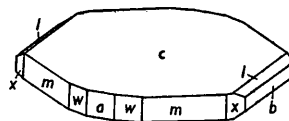


Fig. 3. Change in habit caused by the addition of cupric ions to $(50\text{KK}.50\text{KNa})$ tartrate.

Optical properties

The optical properties of these series of crystals were examined by Buckley (1926) in an earlier paper, and in that work no distinction was made between the composition of the solution and of the solid. This supposition was true for crystals of the following types:

- (i) $(\text{KNa}. \text{NH}_4\text{Na})\text{T}$,
- (ii) $(50\text{KNa}.50\text{KK})\text{T}$ (also with the cupric ion),
- (iii) $(50\text{KNa}.50\text{KNH}_4)\text{T}$,
- (iv) $(80\text{NaNH}_4.20\text{KNH}_4)\text{T}$,

but the mixture $(50\text{NaNH}_4.50\text{NaNa})\text{T}$ commonly crystallized with about $(95\text{NaNH}_4.5\text{NaNa})$ in the solid, although crystals containing up to 39% NaNa were obtained, and the mixture $(50\text{NH}_4\text{Na}.50\text{NH}_4\text{NH}_4)\text{T}$ gave a solid of composition $(94\text{NH}_4\text{Na}.6\text{NH}_4\text{NH}_4)\text{T}$. The volatile nature of the ammonium made it very difficult to obtain solids having a large proportion of ammonium.

Crystals which were found on analysis to be nearly the pure salts (for example, sodium ammonium tartrate) were not greatly different from these in optical characteristics. Where analysis confirmed that the solid was an admixture, optical properties of a widely different type were found. They were especially interesting when all three cations (Na, K, NH_4) were present, in which case a wide 'monoclinic' dispersion of the optic axial planes settled down gradually to a dispersion of orthorhombic, crossed-axial-plane type, in which, by suitable choice of mixture, uniaxial points in any part of the visible spectrum could be obtained.

Electrical properties

The dielectric constant in the $[100]$ direction of pure Rochelle salt, fitted with silver-plated electrodes and measured at 0°C . under a field of 8.75 V.cm^{-1} and at

30 cyc.sec.⁻¹, has been stated by Zeleny & Valasek (1934) to be 3000. Above about 150 kycy.sec.⁻¹ the constant remains steady at about 100, while the constants for the [010] and [001] directions remain universally steady, their values, as given by Mason (1942), being 9.8 and 9.2 respectively.

Evans (1937) measured the inductivities of Rochelle salt modified by the introduction of the ammonium radical and found a sharp drop in the value of the constant for (100) sections even with only a small proportion of ammonium present. The piezo-electric coefficient d_{14} shows a similar sudden drop on the introduction of ammonium (Mandell, 1928).

Present experiments

The inductivities of specimens belonging to the three series of crystals of Rochelle salt type, previously mentioned, were measured between 650 and 2650 kycy.sec.⁻¹ for (100), (010), (001) and a few (210) sections. The field strengths varied, from crystal to crystal, between 44 and 220 V.cm.⁻¹. Thin aluminium electrodes were used, attached to the surfaces of the crystal by a thin layer of Canada balsam. The correction to be applied because of the presence of this layer of binding material, of low inductivity, is given by the relation

$$\beta(d_1 + d_2)/K_0 = \beta(d_1/K_1 + d_2/K_2),$$

in which d_1 and d_2 are respectively the total thicknesses of balsam and crystal, K_0 , K_1 and K_2 respectively the inductivities of (crystal + balsam), balsam alone, and crystal alone, and β is the constant $4\pi/A$. This gives the relation

$$K_2 = K_0 K_1 d_2 / \{K_1(d_1 + d_2) - K d_1\}.$$

It was found that the balsam needed some 2-3 months for complete drying after being applied, and, during this period, a variation of as much as 10% (in the case of (010) and (001) sections) and 5% for (100) sections occurred in the total capacity of the crystal condenser. The final value was always higher than that obtained either when the condenser had just been made or when it was in an intermediate stage; but, after the period of 2-3 months, no further change occurred. It is believed that this point may previously have escaped attention. The crystals were found to keep satisfactorily without the need for coating in wax (Zeleny & Valasek, 1934) provided that they were stored in dry airtight specimen tubes.

The capacity of each crystal condenser was measured at points 50 kycy.sec.⁻¹ apart throughout the range of frequency from 650 to 2650 kycy.sec.⁻¹. Each measured value represented the mean of some eighteen separate determinations at each point, these being designed to detect any variation which might occur with time. Apart from the drying of the balsam, no ageing effect was found. In one instance, certain crystals, prepared in 1924, gave values identical with those of similar crystals prepared in 1947.

Apparatus

Franklin oscillators G_1 and G_2 (see Fig. 4) provided signals of constant amplitude, variable in frequency between 650 and 3100 kycy.sec.⁻¹, which passed through the buffer amplifiers A_1 and A_2 , the mixing stage M and the difference-frequency amplifier A_3 , to one X plate of the cathode-ray oscillograph. A third oscillator, G_3 , controlled by a quartz crystal, provided an output of constant frequency (150 kycy.sec.⁻¹) which was applied to one Y plate of the oscillograph. The other plates of the oscillograph were earthed. It will be appreciated that no time-base was used.

The oscillators G_1 and G_2 ran at frequencies 450 kycy.sec.⁻¹ apart, G_2 being at the higher frequency. The Franklin circuit made a very stable oscillator, and little drift was experienced after the first calibration against a standard signal generator, and a very nearly stationary Lissajous figure could be held for an indefinite time on the cathode-ray oscillograph when the three oscillators were working.

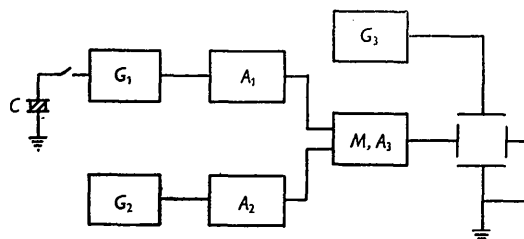


Fig. 4. Block diagram of apparatus used in determining inductivities.

The crystal condenser could be switched across the tuning capacity of G_1 (a Sullivan calibrated standard air condenser), thereby lowering the frequency of the signal from G_1 and destroying the Lissajous figure. This was regained, however, by reducing the capacity of the Sullivan condenser by an amount equal to the capacity introduced by the crystal condenser with its leads. Hence this capacity might be read directly, and after a correction for the stray capacities, and for the presence of the balsam, the inductivity of the crystal could be found.

In order to make it easy to identify the Lissajous figure, often a difficult task if G_1 was well out of tune, a 450 kycy.sec.⁻¹ band-pass filter was fitted in the anode of the mixer stage, so that the voltage supplied to the Y plate of the oscillograph was sharply peaked, and of considerable amplitude, only when the frequencies of the oscillators G_1 and G_2 were 450 kycy.sec.⁻¹ apart, and at this instant also the Lissajous figure was formed by interaction with the 150 kycy.sec.⁻¹ signal from G_3 . All readings of capacity were therefore made at the settings for which the Lissajous figure occurred. The use of this device helped to give greater accuracy, and reduced eye-strain by a large factor.

The crystal was enclosed in an earthed metal box. The rotary switch, used to bring the crystal into circuit,

was mounted on one side of the box, with all contacts inside. In the 'off' position of the switch each electrode was earthed, and the crystal was therefore completely out of circuit. The stray capacities remained constant, and could be determined easily.

Results

(a) Morphological

The important changes which occur on the introduction of impurities have been mentioned earlier, and it only remains to recall the effect of boric acid and of cupric ions in promoting altogether different growths, since a reflexion of this phenomenon occurs in the electrical characteristics.

(b) Electrical

The inductivity of each specimen was found to be constant between 650 and 2650 kcyc.sec.⁻¹, and the mean results for different sections of Rochelle salt and the crystals obtained after the addition of stated impurities are given in Table 1.

It is significant that crystals of Rochelle salt grown with boric acid show both marked changes in growth (no trace of dendrites, and very small inclusions, together with greatly increased toughness) and a 50% drop in inductivity. Certainly the crystal is constrained to grow differently, and there may also be alteration in the size or nature of the domains. Pure Rochelle salt

possesses a well-faceted prism, but when grown with either the cupric ion or boric acid the (210) prism takes its place. The results quoted here for the (210) sections have, so far as is known, never been previously published. They agree with the expectation that the value of the inductivity becomes less as the section is made further away from the (100) direction.

The results in Table 2 refer to the variations of Rochelle salt in which the composition has been altered, and, in two cases, cupric ions have been present as an impurity. It was considered advisable to analyse each of these compounds lest the composition of the crystallized matter had changed at crystallization. In all except two cases, liquid and solid were of identical composition (column 2).

The crystal of composition (50KK.50KNa)T is of outstanding interest in that, when grown in the presence of cupric ions, the inductivity along the (100) directions is nearly 2.5 times as great as it is for the pure crystal in the same direction. The dielectric constants in the (010) and (001) directions are lower in the impure crystal than in the pure crystal. This compound may be contrasted with Rochelle salt itself, which shows a drop in inductivity of only 2%, in the (100) direction, when grown with cupric ions, compared with the value for the pure salt. The (50KK.50KNa) tartrate forms, by itself, prisms which are much the same as those of the pure Rochelle salt, but, when grown with the cupric ion, it

Table 1. *Inductivity of Rochelle salt*

(Inductivities have been corrected for the presence of a layer of balsam.)

Composition	(100)	(010)	(001)	(210)	Reference number
Rochelle salt	94.0	9.6	9.5	†	1
Rochelle salt + cupric ion *	90.0	15.0	11.0	66.6	2
Rochelle salt + 366*	92.0	11.8	13.5	—	3
Rochelle salt + boric acid	49.0	10.2	14.0	36.2	4

* The dyestuff Hessian Yellow.

† Two (100) sections of pure Rochelle salt which had been cut at an angle of 5° towards (110) gave a value of 54.5 for the dielectric constant.

Table 2. *Inductivity of Rochelle salt type crystals of different compositions*

(Inductivities have been corrected for the presence of a layer of balsam.)

Composition of tartrate		Inductivities of sections			Reference number (6)
Solution (1)	Solid (2)	(100) (3)	(010) (4)	(001) (5)	
Rochelle salt	Same	94.0	9.6	9.5	1
Crystals having different proportions of metallic radicals					
33KK.67KNa	Same	50.1	9.7	9.3	5
50KK.50KNa	Same	48.5	13.0	9.2	6
50KK.50KNa + cupric ion	Same	120.0	11.3	8.5	7
Crystals with varying proportions of ammonium present arranged in order of increasing substitution					
80KNa.20KNH ₄	Same	19.2	10.1	9.2	8
50KK.50NaNH ₄	Same	11.4	7.7	9.9	9
50Na ₂ .50NaNH ₄	95NaNH ₄ .5NaNa	10.6	9.9	8.8	10
50Na ₂ .50(NH ₄) ₂	Same	9.2	9.8	11.8	11
50Na ₂ .50(NH ₄) ₂ + cupric ion	Same	14.8	9.0	10.2	12
50KNa.50(NH ₄) ₂	Same	9.2	8.5	9.2	13
80NaNH ₄ .20KNH ₄	Same	8.5	8.8	8.9	14
50NaNH ₄ .50(NH ₄) ₂	94NaNH ₄ .6NH ₄ NH ₄	8.2	8.4	9.2	15
33NaNH ₄ .67NaRb	Same	9.6	8.7	8.6	16

gives flat plates formed on the (001) basal plane (see Fig. 3), the most drastic change of habit recorded in the whole series.

The whole character of the crystals changes with the introduction of the ammonium radical to the molecule (types 8–15 inclusive). One effect of growing ammonium Rochelle salt in the presence of cupric ions is to raise the inductivity in the (100) direction by 60 %, and to reduce its value in the (010) and (001) directions. This invites comparison with the effect in the (50KK.50KNa) tartrate, where there was an increase of 150 % in the (100) direction, and with ordinary Rochelle salt, where a fall of 2 % was recorded in the same direction.

The remaining results show how the inductivity fares when an increasing proportion of ammonium appears in the molecule of Rochelle salt. The smallest replacement occurs in compound (8), and the corresponding inductivity in the (100) direction is reduced to 19.2. The rate at which inductivity in the (100) direction falls with increasing substitution in (KNa)T becomes very much less when more than 10 % of ammonium is present, and the inductivity remains nearly constant after a 25 % substitution has been made. Although the crystal (10) is not strictly derived from (KNa)T, its properties fit the general shape of the relation between percentage substitution and value of inductivity, and the crystal (16) is an example of the replacement of potassium by both ammonium and rubidium, and, again, the relationship is observed.

It is likely that the Canada balsam used for joining the electrodes to the surfaces of the crystal had the effect of damping mechanical vibrations slightly, thereby causing a lower dielectric constant to be read than actually existed. This will account for the difference of

about 6 % which exists between the values quoted here for (100) sections of pure Rochelle salt and those commonly published. Since all the measurements of dielectric constant were made well above resonance frequencies, the crystals did not undergo mechanical movement of large amplitude, and this damping did not become a serious consequence. The layer of balsam was about 0.01 mm. thick, sufficient to require the use of the correction mentioned earlier (p. 335). Each crystal was supported on its lower face only, and the support was at earth potential. The upper face carried the very small masses of the balsam and the electrode, and it is unlikely that stresses occurred in the crystal which would build up piezo-electric charges great enough to influence the results. It appears that the method of plating quartz crystals by sputtering (Spears, 1946) might be extended to Rochelle salt, although this substance readily loses water of crystallization under reduced pressure, and the dehydrated salt is of low inductivity.

One of us (J. H. T.) wishes to thank Dr H. E. Buckley for suggesting the problem, and Prof. P. M. S. Blackett for facilities and encouragement.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1949). **2**, 337

X-ray collimator producing a beam of very small divergence and large intensity.* By J. A. LELY and T. W. VAN RIJSSEL. *Philips Research Laboratories, Eindhoven, Netherlands*

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Using the total reflexion of X-rays at very small glancing angles we have constructed a slit collimator for small-angle diffraction work. We used two slightly divergent plates 10–15 cm. long, leaving apertures of 5–20 μ at the end confronting the X-ray tube, and of 75–150 μ at the other end. The specimen is placed directly behind the wide aperture.

The divergence of the incident radiation is diminished nearly without loss of energy by reflexion from the two highly polished surfaces. The effective angular width α_0 of the incident beam is limited by the critical glancing angle η (Fig. 1).

$\alpha_0 = 2\eta + \beta$, where β is the angle between the polished surfaces. For glass and Cu $K\alpha$ rays $\eta = 14\text{--}15'$, so $\alpha_0 = 30\text{--}34'$ if $\beta = 2\text{--}4'$. The angular width of the emerging beam, α_e , depends on the dimensions of the apparatus and η , and may be easily brought down to 4–6'.

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